Supporting Information for “Coherent Control of Long-range Photoinduced Electron Transfer by Stimulated X-ray Raman Processes”

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Submitted to Proceedings of the National Academy of Sciences of the United States of America

The Effective Hamiltonian

The system is described by the effective Hamiltonian

$$H_s = \sum_{m,n} [t^{(e)}_{mn} c^\dagger_m c_n + t^{(h)}_{mn} v^\dagger_m v_n - W^{(eh)}_{mn} c^\dagger_m v^\dagger_n v_n c_m], \qquad \textbf{[S1]}$$

where m (n) runs over the initially unoccupied (occupied) orbitals. $t^{(e)}_{mn}$ $(t^{(h)}_{mn})$ is the electron (hole) hoping rate, $W^{(eh)}_{mn} = V_{(eh)}(|\mathbf{r}_m - \mathbf{r}_n|)$ is the Coulomb attraction between the electron and the hole. We neglect electron-electron, hole-hole Coulomb repulsion and the dipole-dipole interaction between two excitons at different sites. One can now calculate the matrix elements of the Hamiltonian in Eq. S1 in the three-state basis $(|D'\rangle, |B'\rangle, |A'\rangle)$ using

$$\langle 0 | c_m v_n H_s c^\dagger_k v^\dagger_l | 0 \rangle = \delta_{nl} t^{(e)}_{mk} + \delta_{mk} t^{(h)}_{nl} - \delta_{mk}\delta_{nl} W^{(eh)}_{mn}. \qquad \textbf{[S2]}$$

We assume that the direct electron hoping between donor and acceptor $t^{(e)}_{ba}$ and $t^{(e)}_{ab}$ is weak compared to the donor-bridge hoping $t^{(e)}_{db}$, $t^{(e)}_{bd}$. This is justfied for remote orbitals with a large energy difference - few eV. We further neglect direct hoping of electrons between donor and acceptor such that $t^{(e)}_{da} = t^{(e)}_{ad} = 0$. The Hamiltonian (Eq. S1) $(\hbar = 1)$ can thus be recast as $H_s = H_{DBA} + H_{hop}$ where the diagonal part is given by

$$H_{DBA} = \omega_D |D\rangle\langle D| + \omega_B |B\rangle\langle B| + \omega_A |A\rangle\langle A|, \qquad \textbf{[S3]}$$

and

$$H_{hop} = t_{DB} |D\rangle\langle B| + t_{BA} |B\rangle\langle A| + H.C. \qquad \textbf{[S4]}$$

is the electron hopping Hamiltonian. Here $\omega_D = t^{(e)}_{d,d} + t^{(h)}_{dd} - W^{(eh)}_{d,d}$, $\omega_A = t^{(e)}_{a,a} + t^{(h)}_{dd} - W^{(eh)}_{a,d}$, $\omega_B = t^{(e)}_{b,b} + t^{(h)}_{dd} - W^{(eh)}_{b,d}$ are electronic energies, and $t_{DB} = t^{(e)}_{d,b}$, $t_{BA} = t^{(e)}_{b,a}$ are the hopping rates between many-electron states.

The X-ray parameters are based on the adiabatic (delocalized) basis. By diagonalizing the 3×3 Hamiltonian we obtain the adiabatic exciton Hamiltonian

$$H_s = \omega'_D |D'\rangle\langle D'| + \omega'_B |B'\rangle\langle B'| + \omega'_A |A'\rangle\langle A'|, \qquad \textbf{[S5]}$$

where the exciton basis set is obtained via unitary transformation $U(t)$: $|\{D', B', A'\}\rangle = U(t) |\{D, B, A\}\rangle$.

Electron Transfer Dynamics

Electron transfer dynamics in diabatic basis is described by a master equation (1) where the Liouville space components of the ET rate matrix are

$$K_{DD,DD} = k_{DB}, K_{DD,BB} = -k_{BD}, \qquad \textbf{[S6]}$$

$$K_{BB,DD} = -k_{DB}, K_{BB,BB} = k_{BD} + k_{BA}, K_{BB,AA} = -k_{AB}, \qquad \textbf{[S7]}$$

$$K_{AA,BB} = -k_{BA}, K_{AA,AA} = k_{AB}, \qquad \textbf{[S8]}$$

and the rest of the components are zero. The corresponding Green's function in Liouville space is given by

$$\mathcal{G}_{mn,pq}(t) = -\frac{i}{\hbar}\theta(t) \left[e^{-\mathcal{L}t} \right]_{mn,pq}. \qquad \textbf{[S9]}$$

Eq. (S9) can be recast as

$$\mathcal{G}_{mm,nn}(t) = -\frac{i}{\hbar}\theta(t) \sum_p \chi^R_{mp} (W_{pp})^{-1} e^{-\lambda_p t} \chi^L_{pn}. \qquad \textbf{[S10]}$$

Here, $\chi^{L,R}$ denote the left (right) eigenvectors of the rate matrix K which satisfy the following equations

$$\sum_n \mathcal{K}_{mmnn} \chi^R_{np} = \lambda_p \chi^R_{mp}, \qquad \textbf{[S11]}$$

and

$$\sum_m \chi^L_{pm} \mathcal{K}_{mmnn} = \lambda_p \chi^L_{pn}. \qquad \textbf{[S12]}$$

$W = \chi^L \cdot \chi^R$ and λ_p are the identical eigenvalues for both sets of eigenvectors.

Interaction of the Molecule with X-ray Pulse

The dipole matter-field coupling is formulated in the adiabatic basis. In the interaction picture and the rotating wave approximation (RWA) (1) it reads

$$H'_x(t) = \mathbf{V}'^\dagger(t) \cdot \mathbf{E}(t-T) + \mathbf{V}'(t) \cdot \mathbf{E}^\dagger(t-T), \qquad \textbf{[S13]}$$

where

$$\mathbf{E}(t-T) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \sum_{j=1,2} \mathbf{e}_j \mathcal{E}_j(\omega) e^{-i(\omega+\omega^0_j)(t-T)}, \qquad \textbf{[S14]}$$

and

$$\mathcal{E}_j(\omega) = (2\pi)^{1/2} \sigma_j e^{-\sigma^2_j \omega^2/2 - i\phi_j} \qquad \textbf{[S15]}$$

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is the Gaussian envelope of the component $j = 1, 2$ with pulse bandwidth σ_j and phase ϕ_j. Pulse $\mathbf{E}(t - T)$ has two components tuned such that $\mathcal{E}_1$ nearly resonant with $x - A'$ transition and $\mathcal{E}_2$ - with $x - B'$. These are the positive frequency components of the field centered at delay T, polarization unit vector $\mathbf{e}_j$, center frequency ω_j^0, $j = 1, 2$. $\mathbf{V}'(t) = \sum_{n'=A',B'} \mu_{n'x} e^{-[i\omega_{n'x}+\Gamma_x]t} |n'\rangle\langle x|$ represents a lowering operator that promotes an electron from core orbital x to valence orbital b', a'. The corresponding expression in diabatic basis reads $\mathbf{V}(t) = U(t)\mathbf{V}'(t)U^{-1}(t) = \sum_{n=A,B,D} \mu_{nx} e^{-[i\omega_{nx}+\Gamma_x]t} |n\rangle\langle x|$, which couples all the three diabatic states A, B, D to the core state x. The corresponding generalized polarizability tensor in diabatic basis that originates from X-ray interaction with molecule is given by Eq. (4).

Electron Transfer Control with X-ray Resonant Raman Process

The lowest order correction to acceptor population is linear in X-ray intensity. The corresponding diagram is shown in Fig. S1 (see Ref. (2) for diagram rules). One can read the diagram and obtain

$$\begin{aligned}\Delta P_A(t_1, t_2) = 2\mathcal{R}i\hbar \int_{-\infty}^{t_1+t_2} ds_1 \int_{-\infty}^{s_1} ds_2 \sum_{i,j=1,2} \sum_{m,n,q=A,B,D} \\ \times \mathcal{E}_i^*(s_1 - t_1)\mathcal{E}_j(s_2 - t_1)(\mathbf{e}_i \cdot \mu_{xq})(\mathbf{e}_j \cdot \mu_{xm}) \\ \times \mathcal{G}_{AA,qn}(t_1 + t_2 - s_1)\mathcal{G}_{xn,xn}(s_1 - s_2)\mathcal{G}_{mn,DD}(s_2),\end{aligned} \quad \textbf{[S16]}$$

where $\mathcal{G}_{xn,xn} = -i/\hbar\theta(t)e^{-(i\omega_{xn}+\Gamma_x)t}$, $n = A, B, D$ is a Liouville space greens function that governs core to valence electron dynamics. Under assumption of well separated pulses one can evaluate the time integrals in Eq. (S16) and obtain Eq. (3) in the main text. Here $i = 1$ if $q = A$, $i = 2$ if $q = B$, $j = 1$ if $m = A$ and $j = 2$ if $m = B$.

Parameters for ET Control

In the limit of well separated pulses Eq. 3 in the main text then contains dominant elastic component where $m = n = q = A$

$$\Delta P_{Ael}(t_1, t_2) = 2\mathcal{R}\mathcal{G}_{AA,AA}(t_2)|\mu_{Ax}|^2\sigma_1^2 I_1 \mathcal{G}_{AA,DD}(t_1), \quad \textbf{[S17]}$$

and inelastic correction $q = n = A$, $m = B$

$$\begin{aligned}\Delta P_{Ain}(t_1, t_2) = 2\mathcal{R}\mathcal{G}_{AA,AA}(t_2)\mathcal{G}_{BA,DD}(t_1) \\ \times \mu_{Ax}\mu_{Bx}\sigma_1\sigma_2 I_1^{1/2} I_2^{1/2} e^{-i\phi}.\end{aligned} \quad \textbf{[S18]}$$

The X-ray effect is maximal at $t_2 = 0$ and in the lowest order approximation in the weak B/A coupling we obtain

$$\frac{\Delta P_{Ain}(t_1, 0)}{\Delta P_{Ael}(t_1, 0)} \simeq \frac{\sigma_2^2 I_2^{1/2}}{\sigma_1 I_1^{1/2}} \frac{|\mu_{Bx}|}{|\mu_{Ax}|} \frac{K_{DB}}{K_{BA}} \geq 1. \quad \textbf{[S19]}$$

The inequality (5) in the main text therefore provides an important restriction on the pulse and matter parameters suitable for ET coherent control where the inelastic contribution originated from coherences play an important role. Under assumption of for equal parameters of the both components of the field $I_1 = I_2$, $\sigma_1 = \sigma_2$ Eq. (S19) becomes Eq. (5).

ET Parameter for the Ru-Co Model Complex

From the TDDFT excited state calculation of the Ru-Co model complex, the first valence excited state with significant Ru-to-tpphz character (D→B transition) is the No. 2 excited state with an excitation energy of 2.8013 eV. The significant MOs involved in the transition are shown in Fig. S2. To reduce the computational cost, in the B→A transition calculations, we simply use the $[(^{-}\text{tpphz})\text{Co}^{\text{III}}(\text{CN})_4]^{2-}$ molecular fragment cut from the Ru-Co complex. For this fragment, the first valence excited state with significant tpphz-to-Co character (B→A transition) is the No. 9 excited state with an excitation energy of 2.6070 eV. Thus we choose the following ET parameters: the donor energy 0 eV, the bridge energy $E_B = 2.8$ eV, and the acceptor energy $E_A = 2.8 + 2.6 = 5.4$ eV. The electronic couplings for the D→B and B→A ET process are estimated by using the generalized Mulliken-Hush scheme (3–6):

$$t_{DB,BA} = \frac{\mu_{12}\Delta E_{12}}{\sqrt{(\mu_1 - \mu_2)^2 + 4\mu_{12}}}, \quad \textbf{[S20]}$$

where μ_{12} is the transition dipole between the initial and final states of the ET process; ΔE_{12} is the energy difference of the initial and final states; and $\mu_{1,2}$ are the dipole moments of the initial and final state, respectively. Since the ET direction is along the x axis (see Fig. 1(a) in the main text), we consider only the x-component of the dipole in electronic coupling estimation. For t_{DB}, TDDFT calculations show $\mu_{12} = 1.6137$ a. u., $\Delta E_{12} = 2.7826$ eV, $\mu_1 = 27.0603$ Debye and $\mu_2 = 8.3054$ Debye, so $t_{DB} = 0.557512$ eV; for t_{BA}, TDDFT calculations show $\mu_{12} = 0.0362$ a. u., $\Delta E_{12} = 2.6070$ eV, $\mu_1 = -30.1568$ Debye and $\mu_2 = -60.2611$ Debye, so $t_{BA} = 0.0079674$ eV. Thus we choose $t_{DB} = 0.6$ eV and $t_{DB} = 0.008$ eV. The electron transfer times $k_{DB} = 20$ fs and $k_{BA} = 2$ ps were estimated from the experimental data in Ref. (7). Co 1s core excitation calculations on the simple Co complex fragment show that a typical Co→CN ligand core transition has a transition dipole $\mu_{A'x}^{(x)} = 0$, $\mu_{A'x}^{(y)} = -0.00003$, $\mu_{A'x}^{(z)} = -0.00086$ a. u., and a typical Co→tpphz bridge core transition has a transition dipole $\mu_{B'x}^{(x)} = 0.00033$, $\mu_{B'y}^{(y)} = 0$, $\mu_{B'z}^{(z)} = 0$ a. u., thus we used these numbers in our model simulation. Particle MOs involved in these transitions are shown in Fig. S3.

1. **Louisell WH (1973) Quantum Statistical Properties of Radiation (Wiley, New York).**
2. **Mukamel S, Rahav S (2010) in Advances In Atomic, Molecular, and Optical Physics, eds Arimondo E, Berman P, Lin C (Academic Press) Vol. 59, pp 223–263.**
3. **Cave RJ, Newton MD (1996) Generalization of the Mulliken-Hush Treatment for the Calculation of Electron Transfer Matrix Elements. Chem. Phys. Lett. 249:15–19.**
4. **Mulliken RS (1952) Molecular Compounds and their Spectra. II. J. Am. Chem. Soc. 74:811–824.**
5. **Hush NS (1967) in Progress in Inorganic Chemistry, ed Cotton FA (Interscience Publishers) Vol. 8, pp 391–444.**
6. **Hush N (1968) Homogeneous and Heterogeneous Optical and Thermal Electron Transfer. Electrochim. Acta 13:1005–1023.**
7. **Canton SE, et al. (2015) Visualizing the Non-equilibrium Dynamics of Photoinduced Intramolecular Electron Transfer with Femtosecond X-ray Pulses. Nat. Commun. 6:6359.**

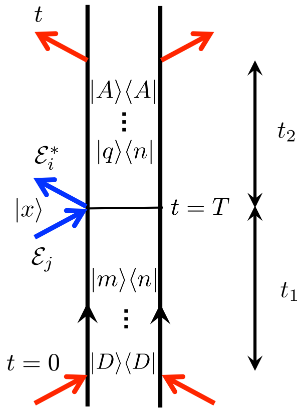

Fig. S1. Ladder diagram corresponding to $\Delta P_A(t_1, t_2)$ (Eq. (3) in the main text). Blue arrows represent interactions with X-ray pulse. Red arrows at $t = 0$ represent photo-induced ET preparation. Red arrows at t correspond to the fluorescence detection of the acceptor population. $|x\rangle$ is the intermediate resonant core state that affects the polarizability α (Eq. (4) in the main text). Diagram rules are presented in (2)

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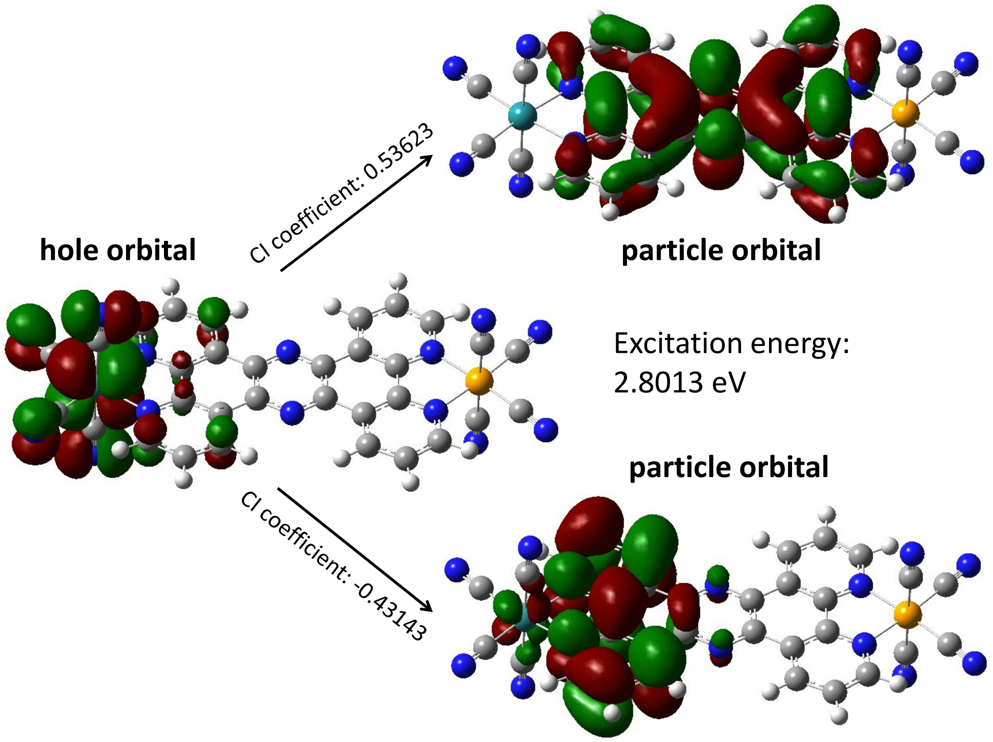
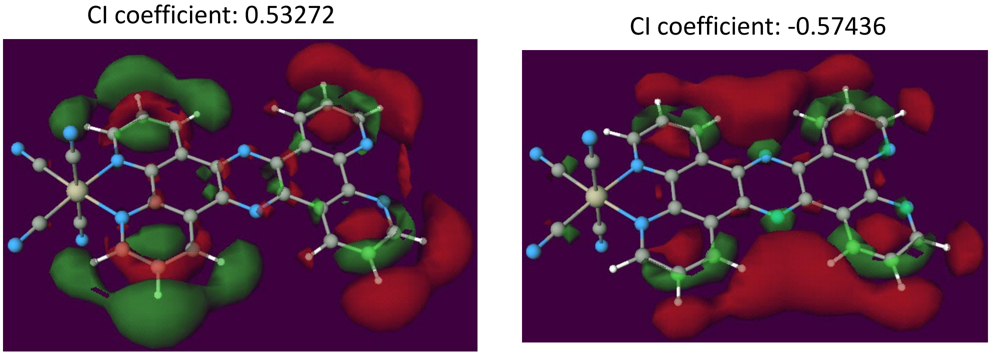
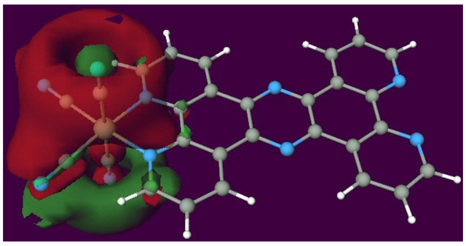


Fig. S2. Representative molecular orbitals of the D⟶B valence excitation of the Ru-Co model complex. The corresponding CI coefficients are also shown. Color code: Ru (light blue), Co (yellow), N (deep blue), C (gray), H (white). Results from TDDFT calculations with Gaussian09.



(a) Excitation energy: 7555.1473 eV



(b) Excitation energy: 7556.6292 eV

Fig. S3. Representative particle molecular orbitals of the B⟶A (a) and A⟶A local core excitation (b) of the simplified Co fragment complex. The corresponding hole orbital is always the Co 1s orbital (not shown). The corresponding CI coefficients are also shown. Color code: Co (light brown), N (blue), C (gray), H (white). Results from restricted excitation window TDDFT calculations with NWChem. Core excitation energies are not shifted.